SAND2014-19158PE

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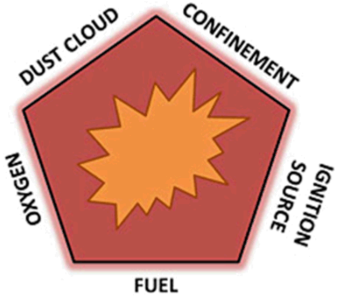

EXPLOSION PENTAGON

Powder Safety Awareness for Additive Manufacturing

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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What are we talking about?

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Dust Hazards:

- Nuisance Dusts:
  - Skin, eye, & respiratory irritants

- Chemical Hazards
  - Toxic Metals
  - Reactive Metal Pairs & Thermites

Cr Ni Cd

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

- Combustible Dusts
  - Fires
  - Dust Deflagrations

U.S. Chemical Safety and Hazard Investigation Board Report No. 2008-05-1-GA, Sept. 2009

Notable combustible dust incidents

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Imperial Refinery; Savannah, GA, 2008; from www.csb.gov

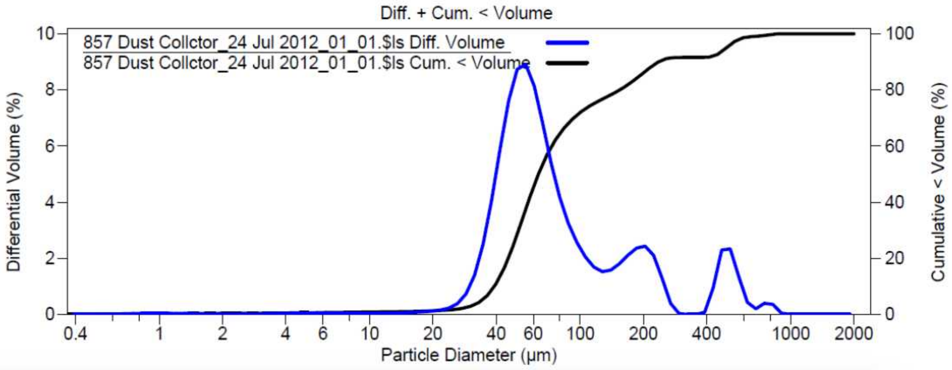
U.S. Chemical Safety and Hazard Investigation Board Report No. 2008-05-1-GA, Sept. 2009

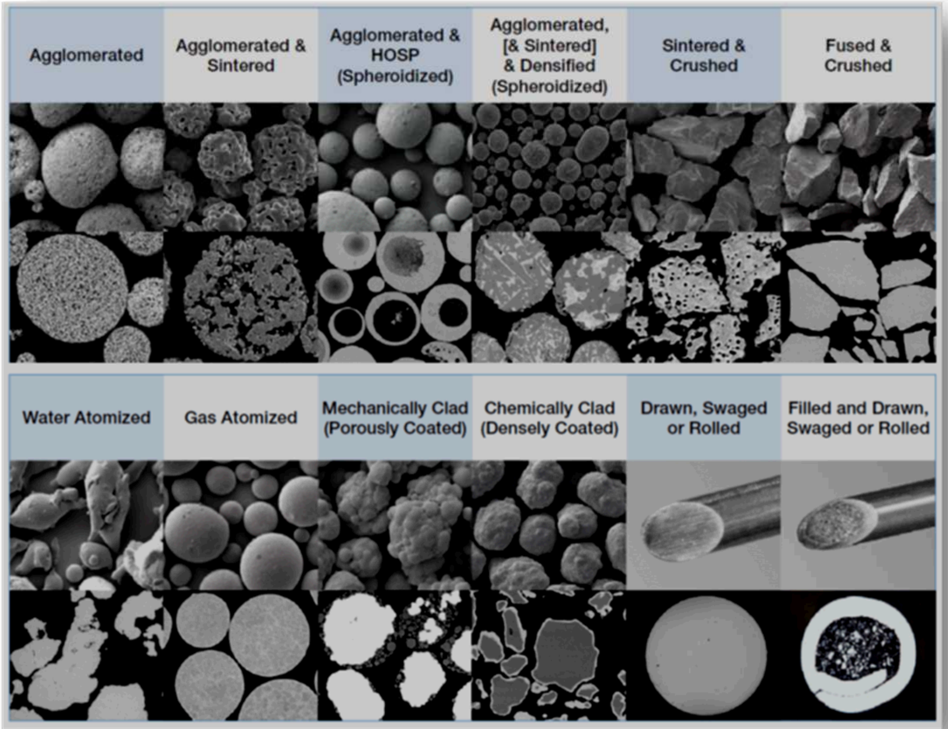
West Pharmaceutical Services, Kinston, NC, 2003; from www.csb.gov

Some Terms & Concepts

- Particle Size
  - All powders have a size.
  - Typically given in microns (e.g. Mean 118.8μm) or sieve size (e.g. -70mesh +325 mesh)
- Particle Size Distribution
  - All powders have a particle size distribution.
  - Particle size distribution can change during processing.
- Particle Morphology
  - Powder morphology is typically directly related to the powder manufacturing process.
  - Can significantly change powder properties (e.g. surface area)

Powders are complex. One powder may be hazardous while another with the same composition may not!

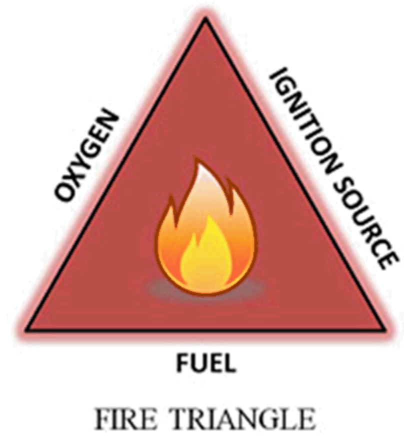




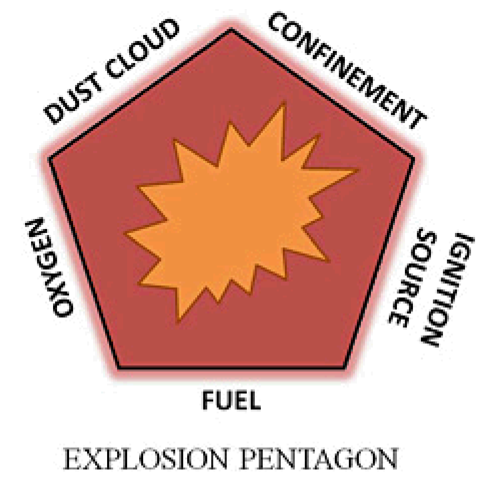
Sulzer-Metco Thermal Spray Materials Guide, Issued April 2014

Some Terms & Concepts

- Dust Fire
  - Simple Combustion
  - Incipient Fires
  - Can sometimes be fought with Class D extinguishers
  - Can lead to deflagration



- Dust Deflagration
  - Dust dispersed in air ignites violently and “explodes”
  - Difficult to achieve, warning signs are often seen.
  - Small dust explosions usually dislodge dust accumulations leading to much larger explosions.



***Dust fires* and *deflagrations* are different things.**

www.usainc.com

http://www.youtube.com/watch?v=bz89_swHtCg

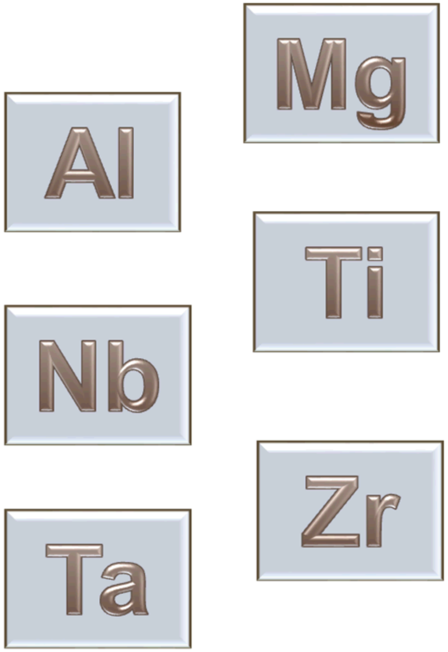
Multiple Fire Codes Apply to Combustible Dusts

- NFPA 484-2012 *Standard for Combustible Metals*
- NFPA 68, Standard on Explosion Protection by Deflagrating Venting
- NFPA 69, Standard on Explosion Prevention Systems
- *NFPA* 654, Standard for the Prevention of Fires and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids
- *NFPA* 61, Standard for the Prevention of Fires and Dust Explosions in Agricultural and Food Processing Facilities
- *NFPA* 655, Standard for Prevention of Sulfur Fires and Explosions
- *NFPA* 664, Standard for the Prevention of Fires and Explosions in Wood Processing and Woodworking Facilities

These Fire Codes are Excellent Sources of Information Regarding Combustible Dusts and How to Handle Them Safely

Particularly Flammable Metals per NFPA-484

- All Alkali Metals
  - Lithium, Sodium, Potassium, Rubidium, Cesium, & Francium
- **Aluminum, Magnesium, & Titanium**
- **Tantalum , Niobium, & Zirconium**
- Alloys of these metals should be considered combustible.
- Dusts from other common metals and alloys can also be combustible; e.g. Zinc, Babbitt, Manganese, Hafnium, Silicon.



Testing is the only way determine if a dust is or is not combustible.

How do I know if my dust is combustible?

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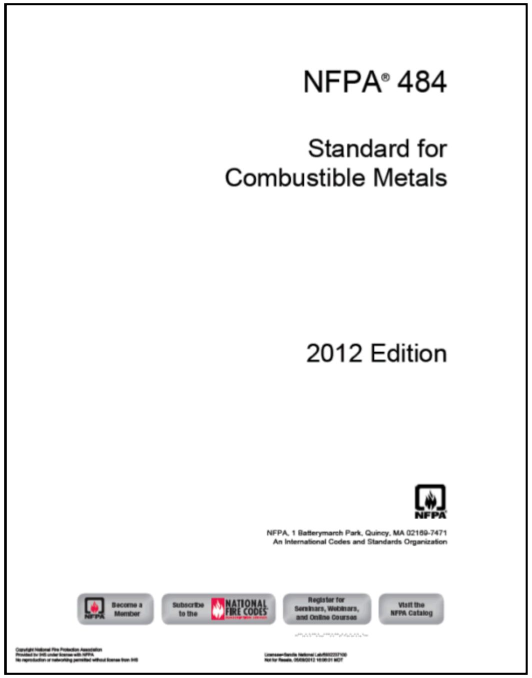
- *"I've worked with this material a lot and it doesn't burn"*
- *"Any particle that has a minimum dimension of less than 500 microns could behave as a combustible dust if suspended in air."* - NFPA 484-2012 A.3.3.6.1
- *"Documentation of noncombustibility proven through analytical testing of combustibility and explosibility of the specific forms of these materials, as described in this chapter and acceptable to the AHJ, is required to eliminate application of this standard."* - NFPA 484-2012 4.1.3
- Combustibility
  - *UN Recommendations on the Transport of Dangerous Goods: Model Regulations — Manual of Tests and Criteria, Part III, Subsection 33.2.1.* - NFPA 484-2012 4.2.1
- Explosibility
  - *ASTM E 1226-12A, Standard Test Method for Explosibility of Dust Clouds.* - NFPA 484-2012 4.3.4


NFPA® 484

Standard for
Combustible Metals

2012 Edition

NFPA, 1 Batterymarch Park, Quincy, MA 02169-7471
An International Codes and Standards Organization

If a material can burn it's dust may be combustible & should be tested. Testing is easy.

How do I evaluate the combustibility of my dust?

- Minimum ignition energy (MIE)
  - Minimum concentration of dust suspended in air, measured in mass per unit volume, which will support a deflagration.
- Maximum pressure (*P*max)
  - The maximum pressure achieved by a deflagration under standard testing conditions.
- Pressure rise (*dP/dt*)
  - The maximum rate of change in pressure during a deflagration.
- **Deflagration index (K_{st})**
  - **The maximum rate of pressure rise during a dust explosion in an equidimensional vessel, multiplied by the cube root of the vessel volume.**
- Limiting oxygen concentration (LOC)
  - Maximum oxygen concentration in a mixture of a flammable substance and air and an inert gas, in which an explosion will not occur, determined under specified test conditions.
- Minimum explosible concentration (MEC)
  - Minimum concentration of dust suspended in air, measured in mass per unit volume, which will support a deflagration.
- Thermal stability, Reactivity, etc…

$$K_{st} = \left({dP}/{dt} \right)_{max} \times \sqrt[3]{V_{vessel}}$$

Dust deflagration index is used to compare the severity of deflagrations caused by different combustible dusts. The value for K_{st} is used to categorize dusts according to the relative violence of their deflagrations.

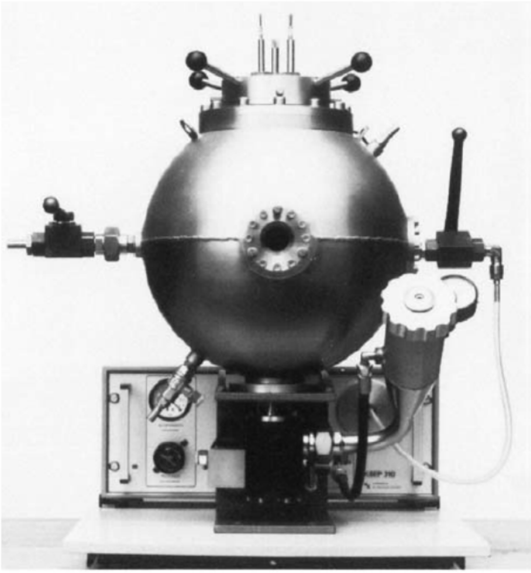
Kst (bar•m/s)	Class	Example
Kst < 200	St. 1 (weak)	Sugar
200 < Kst < 300	St. 2 (moderate)	Wood flour
Kst > 300	St. 3 (strong)	Aluminum powder

Kst is different for every dust and is often used to set boundaries in the code!

http://combustibledust.conversiontechnology.com/terminology.html

Characterizing dust combustibility is complex.

- *Might it explode?*
  - *Laboratory Equipment and Test Procedure for Evaluating Explosibility of Dusts, US Bureau of Mines Report of Investigations 5624*
  - *ASTM-E1226-12A, Standard Test Method for Explosibility of Dust Cloud*
  - ASTM - E789 Standard Test Method for Dust Explosions (Withdrawn 2007). Using this data not recommended
- *Under What Conditions?*
  - *ASTM-E1515, Standard Test Method for Minimum Explosible Concentration of Combustible Dusts*
  - *EN 14034-4, Determination of the Limiting Oxygen Concentration of Dust Clouds*
  - *ASTM-E2019, Standard Test Method for Minimum Ignition Energy of a Dust Cloud in Air*
  - *ASTM-E1491, Standard Test Method for Minimum Autoignition Temperature of Dust Clouds*
  - *ASTM-E2021, Standard Test Method for Hot-Surface Ignition Temperature of Dust Layers*
  - *Prevention of Fires and Explosions in Dryers, Institute of Chemical Engineers, 1990 (Self Heating)*
  - *ASTM-D257 Standard Test Methods for DC Resistance or Conductance of Insulating Materials (Charging)*



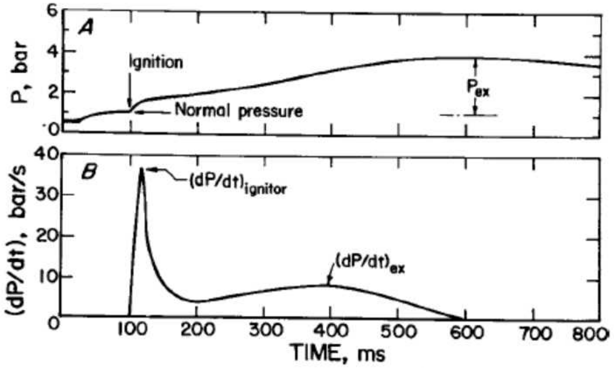


FIG. 3 Typical Recorder Tracings of Absolute Pressure, *P*, and Rate of Pressure Rise, *dP/dt*, for a Weak Dust Deflagration in a 20-L Chamber Using a 5000-J Ignitor

Testing to Assess Explosion Characteristics of Dust Clouds, Vahid Ebadat, Chilworth Technology, NFPA Symposium on Dust Explosion Hazard Recognition and Control, Baltimore, May 13 – 14, 2009

Test conditions matter when evaluating dust hazards!

ASTM-E1226-12A, Standard Test Method for Explosibility of Dust Cloud

- ***With a capacitive discharge spark @ the optimal dust concentration***

ASTM-E1515, Standard Test Method for Minimum Explosible Concentration of Combustible Dusts

- ***Dependent on moisture content and ignition source***

ASTM-E2019, Standard Test Method for Minimum Ignition Energy of a Dust Cloud in Air

- ***With respect to electrostatic discharges @ optimal dust concentration***

ASTM-E1491, Standard Test Method for Minimum Autoignition Temperature of Dust Clouds

- ***Ignition temperature at a concentration and moisture content***

ASTM-E2021, Standard Test Method for Hot-Surface Ignition Temperature of Dust Layers

- ***For layer thickness and times tested***

ASTM-D257 Standard Test Methods for DC Resistance or Conductance of Insulating Materials (Charging)

- ***For the particle size and moisture content tested***

"The values obtained are specific to the sample tested, the method used and the test equipment used. The values are not to be considered intrinsic material constants."

Dust testing is intended to be used a part of a larger hazard assessment.

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"**1.2 Limitations**. _Results_ obtained by the application of the methods of this standard _pertain only to certain combustion characteristics_ of dispersed dust clouds. _No inference should be drawn from such results relating to the combustion characteristics of dusts in other forms or conditions_ (for example, ignition temperature or spark ignition energy of dust clouds, ignition properties of dust layers on hot surfaces, ignition of bulk dust in heated environments, etc.)"

"**1.3 Use**. It is intended that _results_ obtained by application of this test _be used as elements of an explosion risk assessment_ that takes into account _other pertinent risk factors_; and in the _specification of explosion prevention systems_ (see, for example NFPA 68, NFPA 69, and NFPA 654)"

"**13.2.2.2 Warning—**A material classified "not explosible" is _not necessarily non-combustible_. _The same material when exposed to different conditions_, such as elevated temperatures, external heat flux, presence of flammable vapors, size reduction or moisture, _may undergo smoldering, flaming or deflagrative combustion_ either as a dust cloud or as layer."

A negative explosibility result doesn't necessarily mean that there is no hazard!

ASTM-E1226-12A, Standard Test Method for Explosibility of Dust Cloud

Class D Fire Extinguishers are different than other fire extinguishers.

- Class D Extinguishers
  - Aren’t used like Class ABC extinguishers.
  - Deliver Powder that is used to cover and contain the metal fire.
  - Are for fighting small metal fires only.

Fighting a Metal Fire with a Class D Extinguisher – excerpts from NFPA-484

- Size- up the situation and determine if a fire can be safely isolated and allowed to burn out.
- Most fires involving combustible metals cannot be extinguished by covering with Class D agent. The burning material can remain extremely hot, and the fire can flare up if the material is disturbed.
- Large metal fires might be impossible to extinguish. The best approach is to isolate the material as much as possible, if it can be done safely. The fire shall then be allowed to burn itself out naturally to minimize hazards to personnel and losses to equipment.
- Apply dry extinguishing agent carefully so as to avoid any disturbance of the combustible-metal dust, which could cause a dust cloud

Metal fires are difficult and dangerous to fight.

How much dust accumulation is a problem?

- Accumulated dust is fuel sitting around
- Dust accumulated on beams and walls can be disturbed by a small explosion and form a cloud fueling a much larger explosion.
- *1/32" of combustible dust accumulation over 5% of a room's surface area is a hazard*

U.S. Chemical Safety and Hazard Investigation Board Report No. 2008-05-1-GA, Imperial Sugar Company, Sept. 2009

How should we clean up combustible dust?

- Periodic cleanup of fugitive dusts shall be accomplished by using one of the following:
  - (1) Conductive, non-sparking scoops and soft brooms
  - (2) Brushes that have natural fiber bristles
  - (3) Dedicated vacuum cleaning systems designed for handling combustible metal powders used as part of a well defined clean up plan.
- Don't "blow down" equipment with compressed air

Good housekeeping is critical when combustible dusts are involved.

Most Vacuum cleaners should not be used to clean up combustible dusts.

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- Vacuuming a combustible dust presents a fire and explosion hazard in the vacuum cleaner.
  - A Dust Cloud is present inside the vacuum
  - Static charge is formed due to particle motion
- Vacuums specifically designed for combustible dust are available.
  - Immersion separators
  - Pneumatic separators
- Talk to the manufacturer about your situation.

Nilfisk trusted since 1906 | Nilfisk cfm

Industrial Vacuum Division — Nilfisk-Advance, Inc.

Ruwac

Tiger-Vac®

Vacuuming combustible dust is a complex problem!

OSHA Cites 3-D Printing Firm After Explosion

The explosion occurred at the Powderpart company in Woburn, Mass when an employee was using a vacuum to clean up machinery. The vacuum was improperly grounded, which caused a build-up of static charge, igniting dust that caused the explosion".

The employee using the vacuum was critically injured. – *Boston Globe*

The employee suffered 2nd-3rd degree burns on 65% - 70% of his body – *Concord Monitor*

"OSHA has cited 3-D printing firm Powderpart Inc. for one willful violation and nine serious violations after an inspection triggered by a Nov. 5, 2013, explosion and fire. The company faces $64,400 in proposed fines." – *www.eshtoday.com*

The employee was vacuuming titanium powder associated with 3D printing operations.

An explosion proof vacuum was being used but had not been properly maintained.

OSHA Citation and Notification of Penalty #947859; Powderpart, Inc. Woburn, Ma; Issued 5/1/2014

"On or about 11/5/2013, a combustible metal alloy powder fire &/or explosion inflicted life-threatening third-degree burns on the production employee, due to the employer's failure to implement fire &/or explosion preventive and protective measures."

Equipment & Components Involved:

- Concept Laser GmbH M2 3D printer
- TBH GmbH FP 150 EX II 3D De-Duster
- Rofin-Baasel Lasertech GmbH & Co KG 400 watt Fiber Laser
- Ruwac Industriesauger GmbH NA35 Wet Separator
- Concept Laser QM Powder MTF 15 Electronic Vibrator Sieving Station
- Concept Laser GmbH Lifting Device [Hoist]
- Kaeser SM15 Air System (Compressor and Dryer)
- Pressure Tank (1000 L)
- 240 Liter liquid Argon Tank
- Domnick Hunter Division, Parker Hannifin, Ltd MIDIGAS4 Nitrogen Generator

Materials: titanium, aluminum, cobalt chrome, nickel, Inconel, and stainless steel

OSHA Citation and Notification of Penalty #947859; Powderpart, Inc. Woburn, Ma; Issued 5/1/2014

Multiple Serious Violations:

- Employer did not furnish a place of employment free of recognized hazards (combustible dust)
  - Ignition sources present: (no ESD grounding straps & matts)
  - Unreliable oxidant inerting system (no monitoring of inerting gas)
  - Failure to clean dry dust collectors
  - Failure to clean and maintain the wet separator
  - Failure to maintain adequate liquid level in wet separator
  - Failure to appropriately store metal powders (open shelf storage)
- PPE not provided & Hazard Assessments not conducted
  - Failure to provide flame resistant clothing & respiratory protection
- Failure to train employees (hazards and PPE)
- Failure to assess workplace hazards (water sprinklers & metal powders)
- Inadequate safety signs & danger tags (No Smoking signs)
- Equipment and conductors did not meet electrical standards
  - Equipment and wiring not intrinsically safe (Class II, Division 1 electrical panels, light switches, J-boxes, etc.. not present)
  - Electrical boxes not closed
  - Equipment not installed or used per labeling

1 Willful Violation:

- Failure to provide Class D portable fire extinguishers or extinguishing agent.

Reactive Metal Pairs & Thermites

Thermites:

- Metal powder fuel + a metal powder oxide
  - Fuels = Al, Mg, Ti, Zn, Si, B, etc…
  - Oxidizers = Boron Oxide, Silicon Oxide, Chrome Oxide, Manganese Oxide, Iron Oxide, Copper Oxide, Lead Oxide, etc…

$$3CuO + 2Al \rightarrow 3Cu + Al_2O_3$$

Reactive metal pairs:

- Metal powder + Metal powder → Intermetallic + Heat
- Al + Ni   Al + Ti
- Al + B   Ti + B
- Zr + B   Ti + C
- Si-Zr   Co-Si
- Ni-Si   Mn-Si
- Ce-Si   Si-Ti
- & Others!

$$\mathrm{Ni} + \mathrm{Al} \rightarrow NiAl + Heat$$

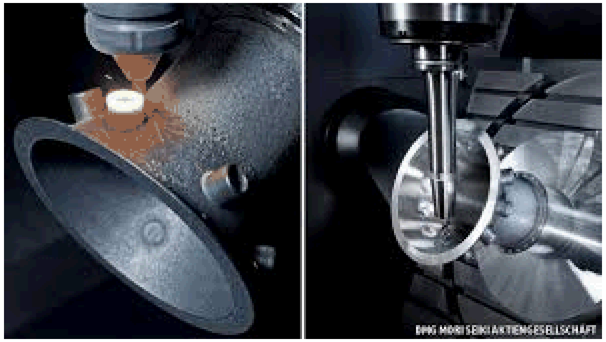
These powder combinations do not require oxygen for "combustion" and will almost always react to completion before they can be extinguished.

SAND98-1176C; S. H. Fischer and M. C. Grubelich; THEORETICAL ENERGY RELEASE OF THERMITES, INTERMETALLICS, AND COMBUSTIBLE METALS

Pyrotechnic Chemistry ISBN 978-1-889526-15-7

Other Food For Thought:

- ***Metal powders cannot be inerted with Nitrogen, CO_2, fluorinated hydrocarbons, or chlorinated hydrocarbons***
  - Magnesium powder will burn under pure N_2, CO_2,or Halon
  - Teflon and aluminum powder will burn
  - Krytox mixed with magnesium powder will burn
- ***There is no upper flammability limit for metal powders***
  - The mix can never be to rich, they will always burn if an oxidizer is available.
- ***Ignition energies are low***
  - Static sparks can ignite most metal dust clouds
- ***Tribocharging can occur easily from particle motion***
  - Grounding is a must in any metal powder system
- ***Many metal powders are water reactive***
  - Al or Mg mixed with water produces H_2 and steam
- ***Damp metal powders can be extremely hazardous***
  - The heat release due to water reaction can produce a powerful steam explosion.
- ***Processing under inert atmosphere can de-passivate a metal powder.***
  - De-passivated powders can auto-ignite when rapidly exposed to air!



Visionaries are proposing making 3D metal printers accessible in office spaces!

Combustible metal dusts are a challenging hazard to manage appropriately!

Good Sources of Information

- http://www.csb.gov/videos/combustible-dust-an-insidious-hazard/
- www.osha.gov/dsg/combustibledust/
- NFPA 484-2012 *Standard for Combustible Metals*
- NFPA Guide to Combustible Dust, 2012 Edition
- ASTM-E1226-12A, Standard Test Method for Explosibility of Dust Cloud
- Other ASTM & NFPA Standards listed above
- Explosibility Of Metal Powders By Murray Jacobson, Austin R. Cooper, And John Nagy United States Department Of The Interior Bureau Of Mines 1964
- SAND98-1176C; S. H. Fischer and M. C. Grubelich; Theoretical ENERGY RELEASE Of Thermites, Intermetallics, and Combustible Metals
- Kenneth L. Cashdollar; Overview Of Dust Explosibility Characteristics, National Institute For Occupational Safety And Health
- Testing to Assess Explosion Characteristics of Dust Clouds, Vahid Ebadat, Chilworth Technology, NFPA Symposium on Dust Explosion Hazard Recognition and Control, Baltimore, May 13 – 14, 2009
- G. Q. Johnson, Preventing Explosions: How to safely clean up combustible dusts, October 2010, PBE

Be Safe & Be Sensible

Fighting a Metal Fire with a Class D Extinguisher – excerpts from NFPA-484

- Size- up the situation and determine if a fire can be safely isolated and allowed to burn out.
- Most fires involving combustible metals cannot be extinguished by covering with Class D agent. The burning material can remain extremely hot, and the fire can flare up if the material is disturbed.
- Large metal fires might be impossible to extinguish. The best approach is to isolate the material as much as possible, if it can be done safely. The fire shall then be allowed to burn itself out naturally to minimize hazards to personnel and losses to equipment.
- Use extreme caution with fires involving combustible metal powders, dusts, and fines. Explosions are possible with these materials, especially if the material becomes airborne with an available ignition source
- Use extreme caution with fires involving large quantities of dust within structures, small dust explosions can aerosolize dust and create much larger explosions.
- Apply dry extinguishing agent carefully so as to avoid any disturbance of the combustible-metal dust, which could cause a dust cloud.
- Do not use pressurized extinguishing agents on a combustible-metal powder fire or chip fire, unless applied carefully so as not to disturb or spread the combustible-metal powder or chip fire.
- Contain small and incipient fires utilizing Class D extinguishing agents, dry sand, or dry salt.
- Ring an incipient fire with a dam of dry sand or dry material that will not react with the metal being extinguished, or with a listed Class D extinguishing powder
- Water in contact with molten combustible metals will result in violent steam and hydrogen explosions and reactions.

Only fight a metal fire if you are certain it is safe to do so.

Some Data on Metal Powders

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Table A.1.1.3(b) Explosibility Properties of Metals

Material	Median Diameter (μm)	K_{st} (bar-m/s)	P_{max} (bar g)	Cloud Ign Temp (°C)	MIE (mJ)	MEC (g/m^3)	UN Combustibility Category[2]	LOC[1] (v%)	Data Source
Aluminum	~7	—	8	—	—	90			Cashdollar & Zlochower[4]
Aluminum	22	—	—	—	—	—	—	5 (N)	BGIA[3]
Aluminum	<44	—	5.8	650	50	45		2 (C)	BuMines RI 6516
Aluminum flake	<44		6.1	650	20	45		<3 (C)	BuMines RI 6516
Aluminum	<10	515	11.2	560	—	60	—	—	BGIA[3]
Aluminum	580	Not Ignited	—	—	—	—	—	—	BGIA
Beryllium	4	Not Ignited	—	—	—	—	—	—	BuMines RI 6516
Boron	<44	—	—	470	60	<100	—	—	BuMines RI 6516
Boron	~3	—	6.0			~110			Cashdollar & Zlochower
Bronze	18	31	4.1	390	—	750	BZ4		Eckhoff
Chromium	6	—	3.3	660	5120	770		14 (C)	BuMines RI 6516
Chromium	3	—	3.9	580	140	230	—	—	BuMines RI 6517
Copper	~30	Not Ignited							Cashdollar & Zlochower
Hafnium	~8	—	4.2	—	—	~180	—	—	Cashdollar & Zlochower
Iron	12	50	5.2	580		500	—		Eckhoff
Iron	~45	—	2.1	—	—	~500	—	—	Cashdollar & Zlochower
Iron	<44	—	2.8	430	80	170	—	13 (C)	BuMines RI 6516
Iron, carbonyl	<10	111	6.1	310		125	BZ3		Eckhoff
Manganese	<44	—	—	460	305	125		—	BuMines RI 6516
Manganese (electrolytic)	16	157	6.3	330	—	—	—	—	Eckhoff
Manganese (electrolytic)	33	69	6.6	—	—	—	—	—	Eckhoff
Magnesium	28	508	17.5	—	—	—	—		Eckhoff
Magnesium	240	12	7	760		500	BZ5		Eckhoff
Magnesium	<44	—	—	620	40	40		—	BuMines RI 6516
Magnesium	<44	—		600	240	30	—	<3 (C)	BuMines RI 6516
Magnesium	~16	—	7.5	—	—	55	—	—	Cashdollar & Zlochower
Molybdenum	<10	Not Ignited							Eckhoff
Nickel	~6	Not Ignited							Cashdollar & Zlochower
Niobium	80	238	6.3	560	3	70		6 (Ar)	Industry
Niobium	70	326	7.1	591	3	50		5 (Ar)	Industry

Different powders behave very differently!

From NFPA 484

What are we doing at the spray lab?

TSRL is installing a new dust collection system designed for combustible metals.

- *Explosive vented, self-cleaning cyclone*
- *>50 ft separation from building*
- *>4500 ft/min transport velocity*
- *Abort dampers in duct work*
- *Fully grounded & Interlocked*

- *New spray hoods with 400 ft/min face velocity*

- *AMEC rated non-sparking fan with bearing temperature sensors*